METHOD FOR CONTROLLING A REFRACTIVE
INDEX OF A DRY PLATING FILM AND
METHOD FOR MAKING A DRY PLATING BUILT-UP FILM

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10 ## BACKGROUND OF THE INVENTION

This invention relates to a method for controlling a
refractive index of a dry plating film wherein a thin film
having a desired refractive index can be reliably made
according to a dry plating process. The invention also
15 relates to a method for making a dry plating built-up film
wherein thin films having different refractive indices are
built up along the thickness thereof to provide a built-up
film suited for use as an optical filter or the like.

Where a desired refractive index is obtained, usual
20 practice is to use an oxide film. However, with an oxide
film, a refractive index does not change significantly by
changing a ratio of oxygen in the oxide film. This places a
limit on the value of refractive index. In addition, it is
difficult to obtain a built-up film whose refractive index
25 is arbitrarily changed as required.

SUMMARY OF THE INVENTION

A first object of the invention is to provide a
method for controlling a refractive index of a dry plating
30 film wherein a thin film having a refractive index ranging
from 1.4 to 2.8 can be reliably made according to a dry
plating process.

A second object of the invention is to provide a
method for simply, reliably making a dry plating built-up
35 film whose refractive index can be arbitrarily changed
along its thickness.

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We made intensive studies in order to achieve the above objects, and as a result, found that when using silicon carbide (SiC) as a target in a sputtering process or as an evaporation source in a vacuum evaporation process and changing the concentration of a reactive gas such as oxygen gas or nitrogen gas, there can be formed a thin film made primarily of SiC wherein the content of carbon is so controlled as to provide an arbitrary refractive index in the range of 1.4 to 2.8 (on measurement at 25°C) depending on the concentration.

According to one embodiment of the invention, there is provided a method for controlling a refractive index of a dry plating film which comprises providing silicon carbide as a starting source and subjecting the silicon carbide to dry plating while controlling a concentration of a reactive gas, thereby forming a thin film, on a substrate, made primarily of silicon carbide and having a refractive index ranging from 1.4 to 2.8.

We also found that when using silicon carbide (SiC) as a target in a sputtering process and changing making electric power against the target, there can be formed a thin film having an arbitrary refractive index in the range of 1.4 to 2.8 (on measurement at 25°C) depending on the making electric power. In this case, when sputtering is carried out while changing the concentration of a reactive gas, such as oxygen or nitrogen gas, there can be more effectively formed a thin film made primarily of SiC and having an arbitrary refractive index.

Thus, according to the second embodiment of the invention, there is provided a method for controlling a refractive index of a sputter film, which comprises providing silicon carbide as a target, and subjecting the silicon carbide to sputtering while controlling electric power charged against a target, thereby forming, on a substrate, a thin film made primarily of silicon carbide which has a refractive index ranging from 1.4 to 2.8.

It has also been found that when dry plating is effected in the first embodiment while changing the concentration of the reactive gas continuously or intermittently, the resultant dry plating film has such a refractive index which is changed in the form of a wave form, such as a rectangular wave, triangular form, sine wave form or the like, along the thickness thereof. Likewise, when sputtering is effected in the second embodiment while changing the electric power against the target continuously or intermittently and, optionally, changing the concentration of a reactive gas continuously or intermittently, the resultant sputtering film has a refractive index which changes in a wave form such as a rectangular, triangular, sine wave or the like form along the thickness thereof. If the film is used as a filter capable of passing an arbitrary band, a built-up film, which is useful as an anti-reflective film such as a visible light anti-reflective film or the like, can be simply formed.

Hence, according to a third embodiment of the invention, there is provided a method for making a dry plating built-up film, which comprises providing silicon carbide as a starting source, and subjecting the silicon carbide to dry plating while changing a concentration of a reactive gas continuously or intermittently, thereby depositing and forming a thin film having different refractive indices along its thickness.

According to a fourth embodiment of the invention, there is provided a method for making a sputter built-up film which comprises providing silicon carbide as a target, and subjecting the silicon carbide to sputtering while changing making electric power against the target continuously or intermittently, thereby depositing and forming a thin film having different refractive indices along its thickness.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing the manner of feed (along a film thickness) of argon and oxygen gases in relation to the variation in time in Example 5;

Fig. 2 is a graph showing the variation in refractive index along a thickness of a built-up film obtained in the above example;

Fig. 3 is a graph showing the manner of feed of oxygen gas in relation to the variation in time in Example 6;

Fig. 4 is a graph showing the variation in refractive index along a thickness of a built-up film obtained in Example 6;

Fig. 5 is a graph showing the manner of feed of argon and oxygen gases in relation to the variation in time in Example 7;

Fig. 6 is a graph showing the variation in refractive index along a thickness of a built-up film obtained in Example 7;

Fig. 7 is a graph showing the manner of feed of argon and oxygen gases in relation to the variation in time in Example 8;

Fig. 8 is a graph showing the variation in refractive index along a thickness of a built-up film obtained in Example 8;

Fig. 9 is a graph showing the variation in making electric power in relation to the variation in time or along a film thickness in Example 11;

Fig. 10 is a graph showing the variation in refractive index along a thickness of the built-up film obtained in Example 11;

Fig. 11 is a graph showing the variation in making electric power in relation to the variation in time in Example 12;

Fig. 12 is a graph showing the variation in refractive index along a thickness of the built-up film obtained in Example 12;

Fig. 13 is a graph showing the variation in making electric power in relation to the variation in time in Example 13; and

Fig. 14 is a graph showing the variation in refractive index along a thickness of the built-up film obtained in Example 13.

DETAILED DESCRIPTION OF THE INVENTION

In the method for controlling a refractive index of a dry plating film and the method for making a dry plating built-up film according to the invention, silicon carbide is provided as a starting source or target and dry-plated on a substrate.

As the dry plating process, there may be used various types of dry plating processes including a sputtering process, a reactive vacuum evaporation process, an ion plating process and the like, and thus, any known ordinary processes may be adopted except that dry plating is carried out in an atmosphere of reactive gases as described hereinafter. Of these dry plating processes, a sputtering process is preferably used.

Although depending on the electric conductivity of a SiC target used, there may be used high frequency sputtering, high frequency magnetron sputtering and the like processes when the electric conductivity is low, and DC sputtering, DC magnetron sputtering and the like processes when the electric conductivity is high. When using a SiC target material which is made of a silicon carbide sintered product and is electrically conductive, DC sputtering and DC magnetron sputtering are preferred.

It will be noted that there may be used, as a substrate, inorganic materials such as glass, ceramics and the like, metal materials, and organic materials such as PMMA, PET and the like.

Silicon carbide is used as a target when a sputtering process is adopted and as an evaporation source when a

vacuum evaporation process is used and also as an
evaporation source in the case of an ion plating process.

Silicon carbide should preferably be one which is
formed as a silicon carbide sintered product obtained by
sintering a mixture having a density of 2.9 g/cm³ or over
and formed by homogeneously mixing silicon carbide powder
and a non-metallic sintering aid. In this case, the total
content of impurities contained in the silicon carbide
sintered product should preferably be not higher than 1 ppm.
The non-metallic sintering aids include organic compounds
capable of producing carbon by heating such as, for example,
coal tar pitch, phenolic resins, furan resins, epoxy resins,
glucose, sucrose, cellulose, starch and the like. Of these,
phenolic resins are preferred. The non-metallic sintering
aid should favorably cover the surfaces of silicon carbide
powder therewith. The silicon carbide sintered product can
be obtained by hot pressing the mixture in a non-oxidative
atmosphere.

The silicon carbide powder used for the preparation
of the silicon carbide sintered product should preferably
be one which is obtained by the following procedure. The
procedure comprises the steps of solidifying a mixture
obtained by mixing a silicon source containing at least one
liquid silicon compound, a carbon source containing at
least one liquid organic compound capable of producing
carbon by heating, and a catalyst for polymerization or
crosslinkage, thermally carbonizing the resultant solid
matter in a non-oxidative atmosphere, and sintering the
matter further in a non-oxidative atmosphere.

The silicon carbide sintered product makes use, as a
sintering aid, of a non-metallic sintering aid alone at the
time of sintering silicon carbide powder without use of a
metallic sintering aid including a metal such as boron,
aluminium, berylium or the like or compounds thereof, or
without a carbon sintering aid such as carbon black,
graphite or the like. Accordingly, the sintered product has
a high purity with a reduced amount of foreign matters

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existing at grain boundaries, and has good thermal conductivity and is inherently better in stain resistance and abrasion resistance than carbon materials. Thus, the silicon carbide is able to form a thin film adapted for use as a protective film or a functional film of various types of electronic device parts and also as a thin film for surface treatment useful in improving the durability of various types of tools.

Accordingly, it is preferred that, in the practice of the invention, the above silicon carbide sintered product is used as a target or an evaporation source.

In the present invention, the control of a refractive index is realized by performing dry plating in a reactive gas atmosphere wherein the concentration of a reactive gas is appropriately controlled (or selected). In the case where a dry plating built-up film having different refractive indexes along the thickness thereof is formed, the dry plating is carried out in a reactive gas atmosphere while changing the concentration of the reactive gas continuously or intermittently.

The reactive gases are not critical in type unless they are inert gases, and include oxygen-containing gases such as oxygen gas, carbon monoxide gas, carbon dioxide gas and like, and nitrogen-containing gases such as nitrogen gas, nitrogen monoxide gas, nitrogen dioxide gas, ammonia gas and the like. These gases may be used singly or in admixture, and oxygen-containing gases and nitrogen-containing gases may be mixed together. If these reactive gases alone are passed into a vacuum chamber, it is preferred to control their concentration within a range of 0 to 100 ml/minute although depending on the capacity of the vacuum chamber. A ratio of the reactive gas to an inert gas (i.e. flow rate of reactive gas/(flow rate of reactive gas + flow rate of inert gas) × 100) is preferably within a range of 0 to 50%.

It will be noted that if a sputtering process is adopted, making electric power may vary depending on the

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size of a target and can be within a range of 50 to 2000 W for a target size of 100 mmϕ, and within a range of 0.5 to 30 W/cm^2 when expressed in terms of a making electric power density in target.

5   The concentration (flow rate) of the reactive gas may be changed continuously or at appropriate intervals of time and is controlled in accordance with a required variation in refractive index. In this way, there can be obtained a film whose refractive index is changed, along its thickness,

10   in a desired wave form such as a rectangular, triangular or sine wave.

     On the other hand, when sputtering is performed using silicon carbide as a target, an arbitrary refractive index can be imparted to the resultant thin film by appropriately

15   controlling (or selecting) making electric power against the target. When the sputtering is carried out while changing the making electric power against the target continuously or intermittently, there can be obtained a sputter built-up film whose refractive index changes along

20   the thickness of the film. In the case, although depending on the size of a target, the making electric power is within a range of 50 to 2000 W for a size of 100 mmϕ and also within a range of 0.5 to 30 W/cm^2 when expressed in terms of making electric power density in target.

25   The sputtering may be effected in an atmosphere of an inert gas such as argon or the like. Although depending on the capacities of a vacuum chamber, a vacuum pump and the like, the flow rate of an inert gas ranges, for example, from 5 to 30 ml/minute, preferably from 10 to 25 ml/minute.

30   In the practice of the invention, a reactive gas may be further incorporated, and when the sputtering is effected while changing the concentration of a reactive gas continuously or intermittently, the refractive index of the resultant thin film can be conveniently controlled. In this

35   case, the reactive gas is not critical with respect to the type thereof provided that it does not consist of an inert gas, and includes oxygen-containing gases such as oxygen

gas, carbon monoxide gas, carbon dioxide gas and the like,
nitrogen-containing gases such as nitrogen gas, nitrogen
monoxide gas, nitrogen dioxide gas, ammonia gas and the
like. These gases may be used singly or in admixture, and
oxygen-containing gases and nitrogen-containing gases may
be used after mixing. Where these reactive gases alone are
passed to a vacuum chamber, their concentration should
preferably be controlled within a range of 0 to 100
ml/minute for an apparatus used in the present invention
although such a range differs depending on the capacities
of a vacuum chamber and a vacuum pump. It is also preferred
that a ratio of the reactive gas to an inert gas (i.e. flow
rate of reactive gas/(flow rate of reactive gas + flow rate
of inert gas) × 100) is within a range of 0 to 50%.

Other sputtering conditions may be those which are
ordinarily employed in this art.

The change in making electric power against a target,
and the change in concentration (flow rate) of a reactive
gas, which is initiated, if necessary, may be effected
continuously or at appropriate intervals of time and is
controlled depending on the required change in refractive
index. In this manner, there can be obtained a film whose
refractive index is changed in a desired wave form, such as
a rectangular wave, triangular wave or sine wave form,
along a thickness thereof.

The thickness of the dry plating film or sputter film
is appropriately selected and is generally in the range of
1 nm to 100 μm, preferably 5 nm to 10 μm.

The dry plating film or sputter film consists of a
film of SiC_xO_y alone (x and y are, respectively, an arbitrary
number) or a film of a mixture of SiC, SiO, SiO_2 and SiC_xO_y
when the reactive gas used is oxygen gas, and a film of
SiC_xN_y alone (x and y are, respectively, an arbitrary number)
or a film of a mixture of SiC, Si_3N_4, SiN and SiC_xN_y when the
reactive gas used is nitrogen gas. The content of carbon is
controlled depending on the concentration of these reactive
gases, and there can be obtained a thin film which is

primarily made of SiC and whose refractive index is arbitrarily changed along the depth thereof within a range of 1.4 to 2.8, preferably 1.46 to 2.67.

The thin film has a refractive index distribution ranging from 1.4 to 2.8 along the depth thereof, and thus, is capable of forming an optical filter which has a high transmittance or a high reflectance within a certain range of wavelength. In addition, the film also has toughness inherent to SiC and can provide a hard coat film which is excellent in abrasion resistance and mar proofing, thus being useful as anti-reflective films, various types of optical filters, transparent, abrasion-resistant films, half mirror films and the like.

EXAMPLE

The invention is more particularly described by way of examples, which should not be construed as limiting the invention thereto.

Example 1

Sputtering was carried out under the following conditions to form thin films having different refractive indices.

Sputtering apparatus: DC magnetron sputtering apparatus

Substrate: glass sheet

Target material: SiC

Target size: 100 mmϕ

Feed gases: argon gas, 18 ml/minute

oxygen gas, flow rates indicated in Table 1

Pressure: 5 mTorr.

Supplied electric power: 500 W

Film-forming time: 10 minutes

Measurement of film thickness: contact type film thickness meter (made by Talor Bobson Inc.)

Measurement of refractive index: Ellipsometry (Nippon Bunko K.K.)

(wavelength for measurement: 800 nm)

Table 1

Flow rate of argon gas	Flow rate of oxygen gas	Making electric power	Refractive index	Film-forming rate (Å/min)
18ml/min	0ml/min	500W	2.00	820
18ml/min	0.2ml/min	500W	2.00	850
18ml/min	1ml/min	500W	1.79	1100
18ml/min	2ml/min	500W	1.58	1280

Example 2

Sputtering was performed in the same manner as in Example 1 except that the making electric power was set at 1000 W, thereby forming thin films having different refractive indices indicated in Table 2.

Table 2

Flow rate of argon gas	Flow rate of oxygen gas	Making electric power	Refractive index	Film-forming rate (Å/min)
18ml/min	0ml/min	1000W	2.67	1500
18ml/min	1ml/min	1000W	2.32	1700
18ml/min	2ml/min	1000W	2.15	1850
18ml/min	5ml/min	1000W	1.73	2600

Example 3

Sputtering was performed in the same manner as in Example 1 except that nitrogen gas was used as a reactive gas in place of oxygen gas and the making electric power was set at 1000, thereby forming thin films having different refractive indices indicated in Table 3.

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Table 3

Flow rate of argon gas	Flow rate of nitrogen gas	Making electric power	Refractive index	Film-forming rate (Å/min)
18ml/min	0ml/min	1000W	2.67	1500
18ml/min	0.2ml/min	1000W	2.62	1510
18ml/min	0.5ml/min	1000W	2.53	1660
18ml/min	1ml/min	1000W	2.52	1600
18ml/min	2ml/min	1000W	2.39	1650
18ml/min	5ml/min	1000W	2.09	2000

Example 4

Reactive vacuum evaporation was conducted under the following conditions to form thin films having different refractive indices. The results are shown in Table 4.

Vacuum evaporation apparatus: electron beam vacuum evaporation apparatus

Substrate: glass sheet

Evaporation source: SiC

Feed gas: oxygen gas, 10 ml/minute

Making electric power against ion source: 500 W

Pressure: 3×10^{-5} Torr.

Film-forming time: 1 minute

Table 4

Making electric power	Refractive index	Film-forming rate (Å/min)
500W	1.65	1350
1000W	2.10	2430
2000W	2.60	4500

The results of these examples revealed that when the concentration (or flow rate) of a reactive gas (i.e. oxygen or nitrogen gas) was appropriately controlled, there could be obtained thin films having different refractive indices.

Example 5

The general procedure of Example 1 was repeated except that sputtering was performed such that an argon gas was continuously fed at a rate of 18 ml/minute while the feed of oxygen gas was turned on or off in a manner as shown in Fig. 1 (with the feed being at 5 ml/minute when the oxygen gas was fed). The resultant film had a change in refractive index as shown in Fig. 2.

Example 6

Sputtering was effected while changing a flow rate of oxygen gas as shown in Fig. 3. The refractive index of the resultant film is shown in Fig. 4.

Example 7

Sputtering was effected while changing a flow rate of oxygen gas as shown in Fig. 5. The refractive index of the resultant film is shown in Fig. 6.

Example 8

Reactive vacuum deposition was effected under the following conditions.
Vacuum evaporation apparatus: electron beam vacuum evaporation apparatus
Substrate: glass sheet
Evaporation source: SiC
Making electric power against ion source: 500 W
Pressure: 3×10^{-5} Torr.
Film-forming time: 1 minute

Sputtering was effected while changing a flow rate of oxygen gas as shown in Fig. 7. The resultant film had a refractive index shown in Fig. 8.

As will be apparent from the foregoing, there can be reliably formed built-up films which had an arbitrary change in refractive index within a range of 1.4 to 2.8 along a thickness thereof.

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Example 9

    Sputtering was effected under the following
conditions to form thin films having different refractive
indices.

5   Sputtering apparatus: DC magnetron sputtering apparatus
    Substrate: glass sheet
    Target material: SiC
    Target size: 100 mmϕ
    Feed gases: argon gas, 18 ml/minute
10   oxygen gas, flow rates indicated in Tables 5 to 7
    Pressure: 5 mTorr.
    Supplied electric power: making powers indicated in Tables
    5 to 7
    Film-forming time: 10 minutes
15 Measurement of film thickness: contact type film thickness
    meter (made by Talor Bobson Inc.)
    Measurement of refractive index: Ellipsometry (Nippon Bunko
    K.K.)

            (wavelength for measurement: 800 nm)

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Table 5

Flow rate of argon gas	Flow rate of oxygen gas	Making electric power	Refractive index	Film-forming rate (Å/min)
18ml/min	0ml/min	100W	1.62	200
18ml/min	0ml/min	300W	1.85	580
18ml/min	0ml/min	500W	2.00	820
18ml/min	0ml/min	700W	2.25	1150
18ml/min	0ml/min	1000W	2.67	1500

Table 6

Flow rate of argon gas	Flow rate of oxygen gas	Making electric power	Refractive index	Film-forming rate (Å/min)
18ml/min	0ml/min	500W	2.00	820
18ml/min	0.2ml/min	500W	2.00	850
18ml/min	1ml/min	500W	1.79	1100
18ml/min	2ml/min	500W	1.58	1280

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Table 7

Flow rate of argon gas	Flow rate of oxygen gas	Making electric power	Refractive index	Film-forming rate (Å/min)
18ml/min	0ml/min	1000W	2.67	1500
18ml/min	1ml/min	1000W	2.32	1700
18ml/min	2ml/min	1000W	2.15	1850
18ml/min	5ml/min	1000W	1.73	2600

Example 10

Sputtering was effected in the same manner as in Example 9 except that nitrogen gas was used, as a reactive gas, in place of oxygen gas (at flow rates indicated in Table 8) and the making electric power was set at 1000 W, thereby obtaining thin films having different refractive indices shown in Table 8.

Table 8

Flow rate of argon gas	Flow rate of nitrogen gas	Making electric power	Refractive index	Film-forming rate (Å/min)
18ml/min	0ml/min	1000W	2.67	1500
18ml/min	0.2ml/min	1000W	2.62	1510
18ml/min	0.5ml/min	1000W	2.53	1660
18ml/min	1ml/min	1000W	2.52	1600
18ml/min	2ml/min	1000W	2.39	1650
18ml/min	5ml/min	1000W	2.09	2000

The results of the above examples reveal that there can be obtained thin films having different refractive indices by controlling the making electric power against the target and further by controlling the concentration (flow rate) of the reactive gas (oxygen or nitrogen gas).

Example 11

Sputtering was effected in the same manner as in Example 10 except that while continuously passing argon gas at a flow rate of 18 ml/minute and oxygen gas at a flow

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rate of 5 ml/minute, the supplied electric power against
the target was changed as shown in Fig. 9. The resultant
film had such a variation in refractive index as shown in
Fig. 10.

Example 12

Sputtering was effected while changing supplied
electric power in a manner as shown in Fig. 11. The
resultant film had a variation in refractive index as shown
in Fig. 12.

Example 13

Sputtering was effected while changing supplied
electric power in a manner as shown in Fig. 13. The
resultant film had a variation in refractive index as shown
in Fig. 14.

As will be apparent from the above examples, there
can be reliably formed built-up films whose refractive
indices are arbitrarily changed within a range of 1.4 to
2.8 along a thickness thereof.